

Claims

- 5     1.     A mass spectrometer comprising:  
          a mass analyser; and  
          a processing system, said processing system being  
          arranged to obtain mass spectral data, to determine a  
          mass to charge ratio of n different species of ion  
10     observed in said mass spectral data and to calculate a  
          respective error band for the determined mass to charge  
          ratio of each of said n different species of ion,  
          wherein the probability or confidence that the real,  
          true, actual or accepted mass to charge ratio of a  
15     species of ion falls within its respective calculated  
          error band is greater than or equal to x%.
2.     A mass spectrometer as claimed in claim 1, wherein  
          n falls within a range selected from the group  
20     consisting of: (i) 1; (ii) 2-5; (iii) 5-10; (iv) 10-15;  
          (v) 15-20; (vi) 20-25; (vii) 25-30; (viii) 30-35; (ix)  
          35-40; (x) 40-45; (xi) 45-50; (xii)  $\geq 50$ ; (xiii)  $\geq 60$ ;  
          (xiv)  $\geq 70$ ; (xv)  $\geq 80$ ; (xvi)  $\geq 90$ ; and (xvii)  $\geq 100$ .
- 25     3.     A mass spectrometer as claimed in claim 1, wherein  
          x falls within a range selected from the group  
          consisting of: (i)  $<1$ ; (ii) 1-5; (iii) 5-10; (iv) 10-15;  
          (v) 15-20; (vi) 20-25; (vii) 25-30; (viii) 30-35; (ix)  
          35-40; (x) 40-45; and (xi) 45-50.
- 30     4.     A mass spectrometer as claimed in claim 1, wherein  
          x falls within a range selected from the group  
          consisting of: (i) 50-55; (ii) 55-60; (iii) 60-65; (iv)

65-70; (v) 70-75; (vi) 75-80; (vii) 80-85; and (viii) 85-90.

5        5.    A mass spectrometer as claimed in claim 1, wherein  
x falls within a range selected from the group  
consisting of: (i) 90-91; (ii) 91-92; (iii) 92-93; (iv)  
93-94; (v) 94-95; (vi) 95-96; (vii) 96-97; (viii) 97-98;  
(ix) 98-99; (x) 99-99.5; (xi) 99.5-99.95; (xii) 99.95-  
99.99; and (xiii) 99.99-100.

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6.    A mass spectrometer as claimed in claim 1, further  
comprising means for reporting the mass to charge ratio  
of at least some of said n species of ion together with  
the respective calculated error band for each mass to  
15    charge ratio.

7.    A mass spectrometer as claimed in claim 1, wherein  
said mass spectral data comprises data relating to the  
time that different species of ion were detected.

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8.    A mass spectrometer as claimed in claim 7, wherein  
said data relating to the time that different species of  
ion were detected is converted into data relating to the  
mass to charge ratio of said ions.

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9.    A mass spectrometer as claimed in claim 8, wherein  
said data relating to the time that different species of  
ion were detected is converted into data relating to the  
mass to charge ratio of said ions by using a calibration  
30    function.

10.   A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of

said n different species of ion said processing system estimates, in use, the systematic error in determining the mass to charge ratio of said ions.

5      11. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
estimates, in use, the accuracy of a mathematical model  
10      used in mass calibration.

12. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
15      said n different species of ion said processing system  
estimates, in use, the error due to mass calibration.

13. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
20      band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
estimates, in use, the error due to using one or more  
internal references or calibrants.

25      14. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
monitors for changes in the time of detection of one or  
30      more internal references or calibrants.

15. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of

said n different species of ion said processing system estimates, in use, the stability or instability of said mass spectrometer subsequent to mass calibration.

5      16. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
estimates, in use, the error due to drift of said mass  
10      spectrometer subsequent to mass calibration.

17. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
15      said n different species of ion said processing system  
estimates, in use, the effect of changes in the  
operating conditions of said mass spectrometer  
subsequent to mass calibration.

20      18. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
estimates, in use, the effect of user intervention  
25      subsequent to mass calibration.

19. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
30      said n different species of ion said processing system  
estimates, in use, the effect of external influences on  
said mass spectrometer subsequent to mass calibration.

20. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
5 estimates, in use, the effect of the stability or  
instability of a power supply of said mass spectrometer  
subsequent to mass calibration.

21. A mass spectrometer as claimed in claim 1, wherein  
10 as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
estimates, in use, the effect of changes in temperature  
on said mass spectrometer subsequent to mass  
15 calibration.

22. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
20 said n different species of ion said processing system  
estimates, in use, the effect of changes in interference  
subsequent to mass calibration.

23. A mass spectrometer as claimed in claim 22, wherein  
25 said interference is due to one or more internal  
reference or calibrant ions interfering with one or more  
analyte ions.

24. A mass spectrometer as claimed in claim 22, wherein  
30 said interference is due to one or more analyte ions  
interfering with one or more internal reference or  
calibrant ions.

25. A mass spectrometer as claimed in claim 22, wherein said interference is due to one or more background or chemical noise ions interfering with one or more internal reference or calibrant ions.

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26. A mass spectrometer as claimed in claim 22, wherein said interference is due to one or more background or chemical noise ions interfering with one or more analyte ions.

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27. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the time elapsed since said mass spectrometer was last calibrated.

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28. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the effect of thermal expansion of one or more components of said mass spectrometer subsequent to mass calibration.

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29. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the error due to space charge repulsion effects within said mass spectrometer.

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30. A mass spectrometer as claimed in claim 29, wherein the error due to space charge repulsion effects is

determined at least in part by consideration of the observed intensity of one or more species of ions.

5 31. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the error recorded during mass calibration.

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32. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error band for the determined mass to charge ratio of each of said n different species of ion said processing system  
15 estimates, in use, the statistical error or random error in determining the mass to charge ratio of said ions.

33. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error  
20 band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the uncertainty or standard deviation of the time of detection of one or more species of ion.

25 34. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the uncertainty or standard deviation  
30 of the frequency of detection of one or more species of ion.

35. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error

band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the error due to ion detection statistics.

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36. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the error due to insufficient sampling.

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37. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the error due to computational errors.

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38. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the error due to rounding off errors.

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39. A mass spectrometer as claimed in claim 1, wherein as part of the process of calculating a respective error band for the determined mass to charge ratio of each of said n different species of ion said processing system estimates, in use, the error in a report exception situation wherein one or more species of ion within said mass spectral data are sufficiently corrupted or suffering from interference that the calculated respective error band of said ions is not reported.

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40. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
5 said n different species of ion said processing system  
estimates, in use, the error due to mass interference  
wherein background or interference ions having  
substantially similar mass to charge ratios to analyte  
ions affect the ability of resolving the analyte ions  
10 from said background or interference ions.

41. A mass spectrometer as claimed in claim 40, wherein  
the error due to mass interference is estimated by  
comparing the shape of an observed mass peak from said  
15 mass spectral data with the shape of a theoretical mass  
peak.

42. A mass spectrometer as claimed in claim 40, wherein  
the error due to mass interference is estimated by  
20 comparing the deviation of the shape of an observed mass  
peak with either a Gaussian distribution, a cosine  
squared distribution, another mathematical function, or  
a profile derived from the shape of one or more mass  
peaks of one or more internal reference or calibrant  
25 ions.

43. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
30 said n different species of ion said processing system  
estimates, in use, the error due to saturation of a  
detector.

44. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
5 estimates, in use, the error due to signal amplification  
saturation.

45. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
10 band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
estimates, in use, the error due to deadtime effects or  
missed counts of an ion counting detector.

46. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
estimates, in use, the error due to the response of an  
20 ion detector.

47. A mass spectrometer as claimed in claim 1, wherein  
as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
25 said n different species of ion said processing system  
estimates, in use, the error due to the response of an  
electron or photon multiplier.

48. A mass spectrometer as claimed in claim 1, wherein  
30 as part of the process of calculating a respective error  
band for the determined mass to charge ratio of each of  
said n different species of ion said processing system  
combines multiple estimates of different errors.

49. A mass spectrometer as claimed in claim 48, wherein said processing system combines said multiple estimates of different errors by adding said estimates in quadrature.

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50. A mass spectrometer as claimed in claim 1, further comprising means arranged to search in use a database to look for one or more ions known to have mass to charge ratios within a range which is related to the determined  
10 mass to charge ratio of one or more ions and the respective calculated error band for the determined mass to charge ratio.

51. A mass spectrometer as claimed in claim 50, wherein  
15 said database comprises details of biopolymers, proteins, peptides, polypeptides, oligionucleotides, oligionucleosides, amino acids, carbohydrates, sugars, lipids, fatty acids, vitamins, hormones, portions or fragments of DNA, portions or fragments of cDNA,  
20 portions or fragments of RNA, portions or fragments of mRNA, portions or fragments of tRNA, polyclonal antibodies, monoclonal antibodies, ribonucleases, enzymes, metabolites, polysaccharides, phosphorolated peptides, phosphorolated proteins, glycopeptides,  
25 glycoproteins or steroids.

52. A mass spectrometer as claimed in claim 50, wherein said database comprises details of the Electron Impact mass spectra of compounds.

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53. A mass spectrometer as claimed in claim 1, further comprising means for calculating elemental compositions having mass to charge ratios within a calculated error

band of the determined mass to charge ratio of one or more species of ion.

54. A mass spectrometer as claimed in claim 53, wherein  
5 said elemental compositions are calculated using the known masses or mass to charge ratios of atomic elements or groups of elements and/or their isotopes.

55. A mass spectrometer as claimed in claim 1, wherein  
10 said processing system is arranged, in use, to define one or more compounds of interest and to interrogate at least some of the determined mass to charge ratios and respective calculated error bands of at least some of  
15 said different species of ion observed in said mass spectral data to see whether said one or more compounds of interest fall within the error band of at least some of said different species of ion.

56. A mass spectrometer as claimed in claim 1, wherein  
20 said processing system is arranged, in use, to define one or more mass to charge ratios of interest and to interrogate at least some of the determined mass to charge ratios and respective calculated error bands of at least some of said different species of ion observed  
25 in said mass spectral data to see whether said one or more mass to charge ratios of interest fall within the error band of at least some of said different species of ion.

57. A mass spectrometer as claimed in claim 1, wherein  
30 said processing system is arranged, in use, to define one or more compounds of interest and to interrogate at least some of the determined mass to charge ratios and respective calculated error bands of

different species of ion observed from a plurality of mass spectra acquired over a period of time to see whether said one or more compounds of interest fall within the error band of at least some of said different species of ion observed from said plurality of mass spectra.

58. A mass spectrometer as claimed in claim 1, wherein said processing system is arranged, in use, to define one or more mass to charge ratios of interest and to interrogate at least some of the determined mass to charge ratios and respective calculated error bands of different species of ion observed from a plurality of mass spectra acquired over a period of time to see whether said one or more mass to charge ratios of interest fall within the error band of at least some of said different species of ion observed from said plurality of mass spectra.

59. A mass spectrometer as claimed in claim 1, further comprising an ion source selected from the group consisting of: (i) an Electrospray ("ESI") ion source; (ii) an Atmospheric Pressure Chemical Ionisation ("APCI") ion source; (iii) an Atmospheric Pressure Photo Ionisation ("APPI") ion source; (iv) a Laser Desorption Ionisation ("LDI") ion source; (v) an Inductively Coupled Plasma ("ICP") ion source; (vi) an Electron Impact ("EI") ion source; (vii) a Chemical Ionisation ("CI") ion source; (viii) a Field Ionisation ("FI") ion source; (ix) a Fast Atom Bombardment ("FAB") ion source; (x) a Liquid Secondary Ion Mass Spectrometry ("LSIMS") ion source; (xi) an Atmospheric Pressure Ionisation ("API") ion source; (xii) a Field Desorption ("FD") ion source; (xiii) a Matrix Assisted Laser Desorption

Ionisation ("MALDI") ion source; and (xiv) a Desorption/Ionisation on Silicon ("DIOS") ion source.

5 60. A mass spectrometer as claimed in claim 1, further comprising a continuous ion source.

61. A mass spectrometer as claimed in claim 1, further comprising a pulsed ion source.

10 62. A mass spectrometer as claimed in claim 1, further comprising a mass analyser selected from the group consisting of: (i) a Time of Flight mass analyser; (ii) a quadrupole mass analyser; (iii) a Penning or Fourier Transform Ion Cyclotron Resonance ("FTICR") mass  
15 analyser; (iv) a 2D or linear quadrupole ion trap; and (v) a Paul or 3D quadrupole ion trap.

63. A method of mass spectrometry comprising:  
obtaining mass spectral data using a mass  
20 spectrometer;  
determining a mass to charge ratio of n different species of ion observed in said mass spectral data; and  
calculating a respective error band for the  
determined mass to charge ratio of each of said n  
25 different species of ion, wherein the probability or confidence that the real, true, actual or accepted mass to charge ratio of a species of ion falls within its respective calculated error band is greater than or equal to x%.

30 64. A method as claimed in claim 63, wherein n falls within a range selected from the group consisting of:  
(i) 1; (ii) 2-5; (iii) 5-10; (iv) 10-15; (v) 15-20; (vi) 20-25; (vii) 25-30; (viii) 30-35; (ix) 35-40; (x) 40-45;

(xi) 45-50; (xii)  $\geq 50$ ; (xiii)  $\geq 60$ ; (xiv)  $\geq 70$ ; (xv)  $\geq 80$ ; (xvi)  $\geq 90$ ; and (xvii)  $\geq 100$ .

5 65. A method as claimed in claim 63, wherein x falls within a range selected from the group consisting of:  
(i)  $<1$ ; (ii) 1-5; (iii) 5-10; (iv) 10-15; (v) 15-20;  
(vi) 20-25; (vii) 25-30; (viii) 30-35; (ix) 35-40; (x) 40-45; and (xi) 45-50.

10 66. A method as claimed in claim 63, wherein x falls within a range selected from the group consisting of:  
(i) 50-55; (ii) 55-60; (iii) 60-65; (iv) 65-70; (v) 70-75; (vi) 75-80; (vii) 80-85; and (viii) 85-90.

15 67. A method as claimed in claim 63, wherein x falls within a range selected from the group consisting of:  
(i) 90-91; (ii) 91-92; (iii) 92-93; (iv) 93-94; (v) 94-95; (vi) 95-96; (vii) 96-97; (viii) 97-98; (ix) 98-99;  
(x) 99-99.5; (xi) 99.5-99.95; (xii) 99.95-99.99; and  
20 (xiii) 99.99-100.

68. A method as claimed in claim 63, further comprising reporting the mass to charge ratio of at least some of said n species of ion together with the respective  
25 calculated error band for each mass to charge ratio.

69. A method as claimed in claim 63, wherein said mass spectral data comprises data relating to the time that different species of ion were detected.

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70. A method as claimed in claim 69, wherein said data relating to the time that different species of ion were detected is converted into data relating to the mass to charge ratio of said ions.

71. A method as claimed in claim 70, wherein said data relating to the time that different species of ion were detected is converted into data relating to the mass to charge ratio of said ions by using a calibration function.

72. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the systematic error in determining the mass to charge ratio of said ions.

73. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the accuracy of a mathematical model used in mass calibration.

74. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to mass calibration.

75. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to using one or more internal references or calibrants.

76. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises monitoring for changes in the time of detection of one or more internal references or calibrants.

77. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises



estimating the stability or instability of said mass spectrometer subsequent to mass calibration.

5 78. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to drift of said mass spectrometer subsequent to mass calibration.

10 79. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the effect of changes in the operating conditions of said mass spectrometer subsequent to mass calibration.

15 80. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the effect of user intervention subsequent to mass calibration.

20 81. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the effect of external influences on said mass spectrometer subsequent to mass calibration.

25 82. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the effect of the stability or instability of a power supply of said mass spectrometer subsequent to mass calibration.

30 83. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the effect of changes in temperature on said mass spectrometer subsequent to mass calibration.

84. A method as claimed in claim 63, wherein the step  
of calculating a respective error band comprises  
estimating the effect of changes in interference  
5 subsequent to mass calibration.

85. A method as claimed in claim 84, wherein said  
interference is due to one or more internal reference or  
calibrant ions interfering with one or more analyte  
10 ions.

86. A method as claimed in claim 84, wherein said  
interference is due to one or more analyte ions  
interfering with one or more internal reference or  
15 calibrant ions.

87. A method as claimed in claim 84, wherein said  
interference is due to one or more background or  
chemical noise ions interfering with one or more  
20 internal reference or calibrant ions.

88. A method as claimed in claim 84, wherein said  
interference is due to one or more background or  
chemical noise ions interfering with one or more analyte  
25 ions.

89. A method as claimed in claim 63, wherein the step  
of calculating a respective error band comprises  
estimating the time elapsed since said mass spectrometer  
30 was last calibrated.

90. A method as claimed in claim 63, wherein the step  
of calculating a respective error band comprises  
estimating the effect of thermal expansion of one or

more components of said mass spectrometer subsequent to mass calibration.

5 91. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to space charge repulsion effects within said mass spectrometer.

10 92. A method as claimed in claim 63, wherein the error due to space charge repulsion effects is determined at least in part by consideration of the observed intensity of one or more species of ions.

15 93. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error recorded during mass calibration.

20 94. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the statistical error or random error in determining the mass to charge ratio of said ions.

25 95. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the uncertainty or standard deviation of the time of detection of one or more species of ion.

30 96. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the uncertainty or standard deviation of the frequency of detection of one or more species of ion.

97. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to ion detection statistics.

5 98. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to insufficient sampling.

10 99. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to computational errors.

15 100. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to rounding off errors.

20 101. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error in a report exception situation wherein one or more species of ion within said mass spectral data are sufficiently corrupted or suffering from interference that the calculated respective error band of said ions is not reported.

25 102. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to mass interference wherein background or interference ions having substantially similar mass to charge ratios to analyte ions affect the  
30 ability of resolving the analyte ions from said background or interference ions.

103. A method as claimed in claim 102, wherein the error due to mass interference is estimated by comparing the

shape of an observed mass peak from said mass spectral data with the shape of a theoretical mass peak.

5 104. A method as claimed in claim 102, wherein the error due to mass interference is estimated by comparing the deviation of the shape of an observed mass peak with either a Gaussian distribution, a cosine squared distribution, another mathematical function, or a profile derived from the shape of one or more mass peaks  
10 of one or more internal reference or calibrant ions.

105. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to saturation of a detector.

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106. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to signal amplification saturation.

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107. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to deadtime effects or missed counts of an ion counting detector.

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108. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to the response of an ion detector.

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109. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises estimating the error due to the response of an electron or photon multiplier.

110. A method as claimed in claim 63, wherein the step of calculating a respective error band comprises combining multiple estimates of different errors.

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111. A method as claimed in claim 110, wherein said multiple estimates of different errors are added in quadrature.

10 112. A method as claimed in claim 63, further comprising searching a database to look for one or more ions known to have mass to charge ratios within a range which is related to the determined mass to charge ratio of one or more ions and the respective calculated error band for  
15 the determined mass to charge ratio.

113. A method as claimed in claim 112, wherein said database comprises details of biopolymers, proteins, peptides, polypeptides, oligionucleotides,  
20 oligionucleosides, amino acids, carbohydrates, sugars, lipids, fatty acids, vitamins, hormones, portions or fragments of DNA, portions or fragments of cDNA, portions or fragments of RNA, portions or fragments of mRNA, portions or fragments of tRNA, polyclonal  
25 antibodies, monoclonal antibodies, ribonucleases, enzymes, metabolites, polysaccharides, phosphorolated peptides, phosphorolated proteins, glycopeptides, glycoproteins or steroids.

30 114. A method as claimed in claim 112, wherein said database comprises details of the Electron Impact mass spectra of compounds.

115. A method as claimed in claim 63, further comprising calculating elemental compositions having mass to charge ratios within a calculated error band of the determined mass to charge ratio of one or more species of ion.

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116. A method as claimed in claim 115, wherein said elemental compositions are calculated using the known masses or mass to charge ratios of atomic elements or groups of elements and/or their isotopes.

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117. A method as claimed in claim 63, further comprising:

defining one or more compounds of interest; and

interrogating at least some of the determined mass

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to charge ratios and respective calculated error bands of at least some of said different species of ion observed in said mass spectral data to see whether said one or more compounds of interest fall within the error band of at least some of said different species of ion.

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118. A method as claimed in claim 63, further comprising:

defining one or more mass to charge ratios of interest; and

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interrogating at least some of the determined mass to charge ratios and respective calculated error bands of at least some of said different species of ion observed in said mass spectral data to see whether said one or more mass to charge ratios of interest fall within the error band of at least some of said different species of ion.

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119. A method as claimed in claim 63, further comprising:

defining one or more compounds of interest; and  
interrogating at least some of the determined mass  
to charge ratios and respective calculated error bands  
of different species of ion observed from a plurality of  
mass spectra acquired over a period of time to see  
whether said one or more compounds of interest fall  
within the error band of at least some of said different  
species of ion observed from said plurality of mass  
spectra.

120. A method as claimed in claim 63, further  
comprising:

defining one or more mass to charge ratios of  
interest; and

interrogating at least some of the determined mass  
to charge ratios and respective calculated error bands  
of different species of ion observed from a plurality of  
mass spectra acquired over a period of time to see  
whether said one or more mass to charge ratios of  
interest fall within the error band of at least some of  
said different species of ion observed from said  
plurality of mass spectra.

121. A mass spectrometer as claimed in claim 63, further  
comprising an ion source selected from the group  
consisting of: (i) an Electrospray ("ESI") ion source;  
(ii) an Atmospheric Pressure Chemical Ionisation  
("APCI") ion source; (iii) an Atmospheric Pressure Photo  
Ionisation ("APPI") ion source; (iv) a Laser Desorption  
Ionisation ("LDI") ion source; (v) an Inductively  
Coupled Plasma ("ICP") ion source; (vi) an Electron  
Impact ("EI") ion source; (vii) a Chemical Ionisation  
("CI") ion source; (viii) a Field Ionisation ("FI") ion  
source; (ix) a Fast Atom Bombardment ("FAB") ion source;



(x) a Liquid Secondary Ion Mass Spectrometry ("LSIMS") ion source; (xi) an Atmospheric Pressure Ionisation ("API") ion source; (xii) a Field Desorption ("FD") ion source; (xiii) a Matrix Assisted Laser Desorption Ionisation ("MALDI") ion source; and (xiv) a Desorption/Ionisation on Silicon ("DIOS") ion source.

122. A mass spectrometer as claimed in claim 63, further comprising a continuous ion source.

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123. A mass spectrometer as claimed in claim 63, further comprising a pulsed ion source.

124. A mass spectrometer as claimed in claim 63, further comprising a mass analyser selected from the group consisting of: (i) a Time of Flight mass analyser; (ii) a quadrupole mass analyser; (iii) a Penning or Fourier Transform Ion Cyclotron Resonance ("FTICR") mass analyser; (iv) a 2D or linear quadrupole ion trap; and (v) a Paul or 3D quadrupole ion trap.

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